

# SELECTIVE HYDRODESULFURIZATION OF 4,6-DIMETHYLDIBENZOTHIOPHENE IN THE MAJOR PRESENCE OF NAPHTHALENE OVER MOLYBDENUM BASED BINARY AND TERTIARY SULFIDES CATALYSTS

Takaaki ISODA\*, Shinichi NAGAO, Xiaoliang MA,  
YOZO KORAI and Isao MOCHIDA

\* Institute of Advanced Material Study, Kyushu University,  
Kasugakouen 6-1, Kasuga, Fukuoka 816, Japan

Keywords : Selective HDS, Ru-CoMo /  $\text{Al}_2\text{O}_3$ , 4,6-dimethyldibenzothiophene

## INTRODUCTION

It has been clarified in previous papers (1) that the sufficient desulfurization of the refractory sulfur species in the diesel fuel such as 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT) should be achieved in its sulfur level of 0.05 % which is currently regulated (2). Such refractory species have been proved to be desulfurized through the hydrogenation of one or both phenyl rings in the substrate to moderate the steric hindrance of methyl groups located in the neighbours of the sulfur atom (3). Hydrogenation of neighboring phenyl rings should competitive with the aromatic partners in the hydrogenation step, being severely hindered (4). The diesel fuel tends to be more aromatic due to crude of more aromaticity and more blending of the craked oil.

In the present study, the catalytic activities of CoMo and NiMo of different contents of Co or Ni and Ru-CoMo /  $\text{Al}_2\text{O}_3$  were examined for the desulfurization of 4,6-DMDBT in decane and decane with naphthalene to find selective catalysts which desulfurize 4,6-DMDBT in the presence of naphthalene through preferential hydrogenation through its phenyl ring. The key step is assumed to be the hydrogenation step of 4,6-DMDBT in the competition with naphthalene. Ru was the selected as the third component of metal promoter which was added to CoMo /  $\text{Al}_2\text{O}_3$ , since sulfur atom in 4,6-DMDBT can be a preferable anchor to the noble metal sulfide in competition with the aromatic hydrocarbon (5-6). Characterization of Ru-CoMo /  $\text{Al}_2\text{O}_3$  using XPS, XRD and HR-EM to find the origin of the selectivity for the desulfurization in the aromatic hydrocarbons.

## EXPERIMENTALS

**Chemicals and Catalysts** ; 4,6-DMDBT was synthesized according to the reference (7). Commercially available  $(\text{NH}_4)_2\text{MoO}_4$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  were used as catalyst precursor salts. Commercially available  $\text{Al}_2\text{O}_3$  was selected as the catalyst support.

The precursor salt was impregnated onto  $\text{Al}_2\text{O}_3$  according to an incipient wetness impregnation procedure. Impregnation additives such as HCl,  $\text{H}_3\text{PO}_4$ , malic acid and citric acid are used in the impregnation solution. Contents of metal oxides supported were as follows; Co(0 - 3 wt%)-Mo(15 wt%) /  $\text{Al}_2\text{O}_3$ , Ni(0 - 5 wt%)-Mo(15 wt%) /  $\text{Al}_2\text{O}_3$ , Ru(0.75 wt%)-Co(0.25wt%)-Mo(15 wt%) /  $\text{Al}_2\text{O}_3$ , respectively.

After the impregnation, the catalyst was dried at 160°C, calcined at 420°C under air flow, and presulfurized at 360°C for 2h by flowing  $\text{H}_2\text{S}$  (5vol %) in  $\text{H}_2$  under atmospheric pressure just before its use.

**Reaction** ; HDS of 4,6-DMDBT in decane with naphthalene was performed in a 50 ml batch-autoclave at 300°C under 2.5MPa  $\text{H}_2$  pressure for 0.5 - 2.5h, using 1.5g catalyst and 10g substrate including solvent. The concentrations of 4,6-DMDBT and naphthalene were 0.1 and 10 wt %, respectively. After the reaction, products were qualitatively and quantitatively analyzed by GC-MS, GC-FID (Yanaco G-3800 and G-100) and GC-FPD(Yanaco G-3800 and 50ml OV-101).

**XPS** ; X-ray photoelectron spectra (XPS) was taken on a ESCA 1000 (Shimadzu co.) with Mg  $K_{\alpha}$  radiation energy of 1253.6 eV. The binding energy was identified according to the references (8-11).

**XRD** ; X-ray diffraction (XRD) was taken on a X-ray diffraction meter (Rigaku co.) with Cu target electrode at 40 KV voltage. X-ray diffraction was performed according to the procedure described by International Center for Diffraction Data (12).

**HREM** ; High resolution electron micrographs (HREM) of catalysts were taken on JEM -2000 EX (Jeol co.) at 200 KV acceleration voltage at magnification of 150 to 500K.

## RESULTS

### Inhibition with Naphthalene of HDS Reaction over NiMo and CoMo catalysts

Fig.1(A) illustrates HDS activity of NiMo catalysts for 4,6-DMDBT in decane and decane with 10 wt% naphthalene at 300°C under 2.5MPa H<sub>2</sub> for 2h. The catalysts gave 95 - 100% conversion of 4,6-DMDBT in decane regardless of Ni content which increased very much the desulfurization compared to that over Mo / Al<sub>2</sub>O<sub>3</sub> in decane. Naphthalene of 10 wt% reduced the conversion to 45% on Mo / Al<sub>2</sub>O<sub>3</sub> and Ni(1)-Mo / Al<sub>2</sub>O<sub>3</sub>, and 77% on Ni(5)-Mo / Al<sub>2</sub>O<sub>3</sub>. Significant retardation by naphthalene was observed over Ni-Mo / Al<sub>2</sub>O<sub>3</sub> especially when Ni content was low.

Fig.2 shows the HDS products from 4,6-DMDBT over Mo and NiMo / Al<sub>2</sub>O<sub>3</sub>. NiMo / Al<sub>2</sub>O<sub>3</sub> produced B<sub>4,6</sub> as the major product and A<sub>4,6</sub> as the second major while Mo / Al<sub>2</sub>O<sub>3</sub> did A<sub>4,6</sub> as the major and B<sub>4,6</sub> as the second major in decane. Overall desulfurization was certainly enhanced by addition of Ni through the hydrogenation. Naphthalene of 10 wt% reduced very much the desulfurization over Mo / Al<sub>2</sub>O<sub>3</sub> and Ni(1)-Mo / Al<sub>2</sub>O<sub>3</sub>. Mo / Al<sub>2</sub>O<sub>3</sub> and Ni-Mo / Al<sub>2</sub>O<sub>3</sub> with less content of Ni suffered large reduction of both products by 10 wt% naphthalene. Large amount of Ni increased the B<sub>4,6</sub> overcoming the inhibition of naphthalene while A<sub>4,6</sub> suffered very much the retardation regardless of Ni content.

Fig.1(B) shows conversion of naphthalene to tetralin and decalin. Ni of 1 wt% or more addition accelerate very much the hydrogenation of naphthalene, giving 100% tetralin and 25% decalin, while Mo / Al<sub>2</sub>O<sub>3</sub> provided 80% conversion to tetralin without decalin.

Table 1 summarizes the yield of minor products, hydrogenated one (H) and desulfurized one without hydrogenation (C<sub>4,6</sub>). Addition of Ni increased the yield of C<sub>4,6</sub> and reduced that of H.

Fig.3(A) illustrates the HDS of 4,6-DMDBT over CoMo / Al<sub>2</sub>O<sub>3</sub> in decane and decane with 10 wt% naphthalene. The CoMo catalysts allowed 100% conversion of 4,6-DMDBT regardless of Co content under the present conditions in decane. Naphthalene of 10 wt% reduced the conversion to 75% in Co(0.25)Mo / Al<sub>2</sub>O<sub>3</sub>, 87% over Co(1)Mo / Al<sub>2</sub>O<sub>3</sub>, and 68% over Co(3)Mo / Al<sub>2</sub>O<sub>3</sub>. It should be noted that Co(1)Mo / Al<sub>2</sub>O<sub>3</sub> suffered the smallest retardation by naphthalene.

Fig.4 shows yields of products from 4,6-DMDBT over CoMo / Al<sub>2</sub>O<sub>3</sub> of different Co contents. B<sub>4,6</sub> was the major product, of which yield increased markedly by addition of Co to Mo, reaches the maximum of 80% by Co of 1wt% in decane and 60% in decane with 10 wt% naphthalene. Addition of Co increased very sharply the yield of B<sub>4,6</sub> the major product, 1 wt% of Co giving the maximum yield. A<sub>4,6</sub> the second major product, was produced most over Mo / Al<sub>2</sub>O<sub>3</sub>. Addition of Co reduced it sharply in decane. Yield of A<sub>4,6</sub> decreased markedly in decane with 10% naphthalene over Mo / Al<sub>2</sub>O<sub>3</sub>, while addition of 0.25 and 1 wt% of Co slightly increased it.

### Activity of Ru-CoMo / Al<sub>2</sub>O<sub>3</sub>

Fig.5 (A) illustrates HDS conversion of 4,6-DMDBT in decane or decane with 10wt % naphthalene over Ru(0.75 wt%) added Co(0.25 wt%)-Mo, Co(3 wt%)-Mo and Ni (5 wt%)-Mo / Al<sub>2</sub>O<sub>3</sub>, respectively, by 2h. High HDS conversions of 95 - 100 % were obtained over all three catalysts in decane. Naphthalene of 10 wt% in decane reduced the HDS conversion over the catalysts, however the extent reduction depended in the amounts of Co or Ni. Co content of 0.75 wt% exhibited 22% reduction while Co and Ni of 3 and 5 wt% severe suffered 30 and 39 % reduction, respectively.

Hydrogenation conversion of coexistent naphthalene is shown in Fig.5 (B). Ru-NiMo / Al<sub>2</sub>O<sub>3</sub> provide the highest conversions of naphthalene to tetralin and decalin of 100% and 20%, respectively, while the conversions were 90% and 10%, respectively, over Ru-Co(0.25 wt%)-Mo / Al<sub>2</sub>O<sub>3</sub>. Hence, Ru-CoMo / Al<sub>2</sub>O<sub>3</sub> with 0.25 wt% Co exhibited the highest HDS activity of 4,6-DMDBT by minimum hydrogenation of co-existence naphthalene.

### Hydrodesulfurization and Hydrogenation Selectivities

Fig. 6 compares the conversions of 4,6-DMDBT hydrodesulfurization and naphthalene hydrogenation over NiMo, CoMo and additive with Ru(0.75 wt%)-Co(0.25 wt%)-Mo(15 wt%) / Al<sub>2</sub>O<sub>3</sub> at 300°C for 0.5h and 2h where 0.1 wt% 4,6-DMDBT and 10 wt% naphthalene were present in decane. There were found two kinds of the catalysts: one exhibited a larger conversion of naphthalene with much less conversion of 4,6-DMDBT, and the others were large conversions of 4,6-DMDBT. The first group of catalyst contained NiMo, the second one contained Ru-CoMo and Ru-CoMo with additive H<sub>3</sub>PO<sub>4</sub> and HCl.

In order to compare the reaction selectivity between the HDS for sulfur compound and hydrogenation (HGN) for aromatic hydrocarbon, relative selectivity was introduced according to the equation (1). Selectivity ratio is shown as follows:

$$\text{Selectivity ratio of 4,6-DMDBT} = \frac{(\text{Reaction mole ratio of 4,6-DMDBT over NiMo / Al}_2\text{O}_3 \text{ or Ru-CoMo / Al}_2\text{O}_3)}{(\text{Reaction mole ratio of 4,6-DMDBT over CoMo / Al}_2\text{O}_3)} \quad (1)$$

Fig. 7 shows the selectivity ratio of 4,6-DMDBT calculated from data of Fig. 6 versus conversion of naphthalene. It clarified hydrogenation activity for naphthalene decreased with increasing the selectivity ratio of 4,6-DMDBT over these catalysts. Particular Ru-CoMo-HCl / Al<sub>2</sub>O<sub>3</sub> showed the highest hydrodesulfurization selectivity for 4,6-DMDBT, giving ratio of 1.41, while giving ratio of 1.28, 1.12 and 1.0 over Ru-CoMo / Al<sub>2</sub>O<sub>3</sub>, Ru-CoMo-P / Al<sub>2</sub>O<sub>3</sub> and CoMo / Al<sub>2</sub>O<sub>3</sub>, respectively. NiMo / Al<sub>2</sub>O<sub>3</sub> was inferior to CoMo / Al<sub>2</sub>O<sub>3</sub> for hydrodesulfurization selectivity of 4,6-DMDBT, giving ratio of 0.38. Especially, Ru-CoMo-HCl / Al<sub>2</sub>O<sub>3</sub> showed as 1.7 times higher selectivity for hydrodesulfurization of 4,6-DMDBT as that of NiMo / Al<sub>2</sub>O<sub>3</sub>, while 0.4 times lower hydrogenation activity of naphthalene.

### XPS Analysis

Fig. 8 shows XPS of Mo 3d in the Ru(x)-Co(y)-Mo(15wt%) / Al<sub>2</sub>O<sub>3</sub> (0 ≤ x, y ≤ 1 wt %) catalysts before and after presulfiding. Before sulfiding, two Mo 3d<sub>3/2</sub> and 3d<sub>5/2</sub> peaks were found at 235 and 232 eV of binding energies (8-11), indicating MoO<sub>3</sub> species in all catalysts regardless of their compositions. Sulfiding sharply the peaks to 225 and 222 eV, respectively in Mo / Al<sub>2</sub>O<sub>3</sub> and CoMo / Al<sub>2</sub>O<sub>3</sub>, indicating the Mo(II) species (8-11). Ru-CoMo / Al<sub>2</sub>O<sub>3</sub> and Ru-Mo / Al<sub>2</sub>O<sub>3</sub> exhibited two peaks at 222 and 218 eV with a very small peak at 225 eV, indicating major presence of Mo 3d<sub>5/2</sub> of Mo(0) at 218 eV after the sulfiding. These results indicated two kinds of Mo species, such as MoS<sub>2</sub> and metal Mo existed on sulfided Ru-CoMo / Al<sub>2</sub>O<sub>3</sub> catalyst.

### XRD Analysis

Fig. 9 shows XRD spectra of a series of Ru(x)-Co(y)-Mo(15 wt%) / Al<sub>2</sub>O<sub>3</sub> (0 ≤ x, y ≤ 1 wt %) before presulfiding. There were two large peaks ascribed to alumina of 45.7° and 66.5°, respectively, with all catalysts. Three sharp peaks were identified with MoO<sub>3</sub> of 23.4°, 25.6° and 27.3°, respectively, over the Mo based on catalysts. The intensity of these three peaks increased with increasing content of Ru on CoMo / Al<sub>2</sub>O<sub>3</sub> indicating the large crystals of MoO<sub>3</sub> in the presence of Ru. The peaks of 33.7° and 53.9° were identified to RuO<sub>2</sub>, while no peak was ascribed to Co oxide. No definite peaks related to Mo, Ru and Co species were found after the sulfiding.

### HREM

Fig. 10 shows HREM micrographs of sulfided Ru(0.75 wt%)-Co(0.25 wt%)-Mo(15 wt%) / Al<sub>2</sub>O<sub>3</sub>. Fig. 10 (a) and (b) shows MoS<sub>2</sub> layers and RuS<sub>2</sub> crystals as dotted spots, respectively, under 20K magnification which were typically observed on Ru-CoMo / Al<sub>2</sub>O<sub>3</sub>. Large magnification of (a) under 50K clarified large length and thickness of MoS<sub>2</sub> layers.

### DISCUSSION

Fig. 11 illustrates the reaction pathway of 4,6-DMDBT in decane over Mo sulfide based on catalysts. There were two desulfurization routes, one is the desulfurization through the hydrogenation of one phenyl group; i.e., hydrodesulfurization route, and the other is desulfurization without apparent hydrogenation; i.e., direct-desulfurization route. The former reaction route is strongly hindered by the dominant presence of naphthalene.

In earlier works, it has been proposed desulfurization active site of sulfided CoMo and NiMo catalysts were anion-vacancy at edge plane of  $\text{MoS}_2$  (13). Voorhoeve and Stuver proposed "Intercalation model" which Ni and Co located edge plane of  $\text{MoS}_2$  (14), Delmon proposed "Contact synergy model" which high activity brought contact between tiny  $\text{Co}_8\text{S}_9$  and  $\text{MoS}_2$  crystal (15), and Topsøe insisted the mechanism of high activity by "Co-Mo-S phase model" which located on edge plane of  $\text{MoS}_2$  (16). Additive co-catalysts, such as Ni or Co brought the high activity of  $\text{MoS}_2$ .

The role of Ru addition to Mo sulfide based on catalysts are classified two categories, reduction of hydrogenation activity for aromatic hydrocarbon and promotion of hydrogenation selectivity for sulfur compound. In addition XPS spectra indicated additive Ru in CoMo catalyst was easily reduced  $\text{MoS}_2$  to metal Mo. Hence hydrogenation activity of aromatic hydrocarbon was controlled by additive Ru, and it suggests competitive reaction of 4,6-DMDBT with naphthalene on hydrogenation active site was relieved. Crystals of  $\text{RuS}_2$  and (Co)- $\text{MoS}_2$  were found existing separately by HREM, it may be suggest 4,6-DMDBT takes precedence over the hydrogenation of naphthalene on the  $\text{RuS}_2$ , and hydrogenated 4,6-DMDBT was completely desulfurized over (Co)- $\text{MoS}_2$ .

In order to design of the higher selective hydrodesulfurization catalyst, it will be necessary to high dispersion of Ru on the surface of support, and optimization of the amount of CoMo and Ru on catalyst. Other side of the aspect, it will be worthwhile to try the hybridization of  $\text{Ru} / \text{Al}_2\text{O}_3$  and  $\text{CoMo} / \text{Al}_2\text{O}_3$ .

#### LITERATURE CITED

- (1) Isoda, T., Ma, X., Mochida, I., *J.Jpn. Pet. Inst.*, **37**, 368 (1994).
- (2) Takatuka, T., Wada, Y., Suzuki, H., Komatsu, S., Morimura, Y., *J.Jpn. Pet. Inst.*, **35**, 197 (1992).
- (3) Isoda, T., Ma, X., Mochida, I., *J.Jpn. Pet. Inst.*, **37**, 506 (1994).
- (4) Isoda, T., Ma, X., Nagao, S., Mochida, I., *J.Jpn. Pet. Inst.*, **38**, 25 (1995).
- (5) Isoda, T., Kisamori, M., Ma, X., Mochida, I., Abstract of Symposium on Jpn. Pet. Inst., p.42, 17 - 18 May 1994, Japan.
- (6) Isoda, T., Ma, X., Nagao, S., Mochida, I., Abstract of Symposium on Jpn. Pet. Inst., p.316, 26 - 27 Oct. 1994, Japan.
- (7) Gerdil, R., Lucken, E., *J.Am. Chem. Soc.*, **87**, 213 (1965).
- (8) Chung, P.L., David, M.H., *J. Phys. Chem.*, **88**, 456 (1984).
- (9) Gajardo, P., Mathieux, A., Grange, P., Delmon, B., *Appl. Catal.*, **3**, 347 (1987).
- (10) Walton, R.A., *J. Catal.*, **44**, 488 (1976).
- (11) Ledoux, M.J., Hantzer, S., Guille, J., *Bull. Soc. Chem. Belge.*, **96**, 855 (1987).
- (12) International centre for diffraction data, "Inorganic Phases", (1989).
- (13) Prins, R., De Beer, V.H.J., Somorjai, G., *Catal. Rev. Sci. Eng.*, **31**, 1 (1989).
- (14) Voorhoeve, R.J.H., Stuver, J.C.M., *J. Catal.*, **23**, 228 (1971).
- (15) Grange, P., Delmon, B., *J. Less Common Met.*, **36**, 353 (1974).
- (16) Topsøe, N.Y., Topsøe, H., *J. Catal.*, **84**, 386 (1983).

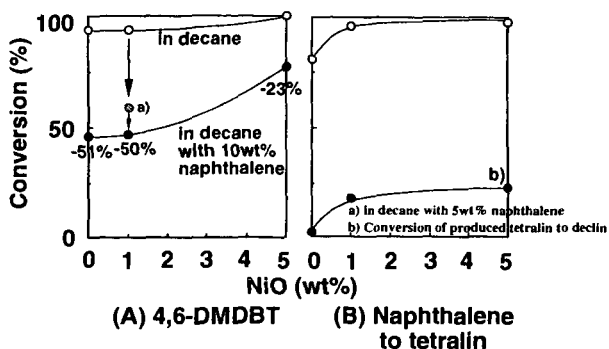


Fig.1 Inhibition with naphthalene of HDS reaction over NiMo catalysts. (300°C-2.5MPa, 4,6-DMDBT 0.1wt% + Nap 10wt% in decane, Catalyst content; 15 wt%)

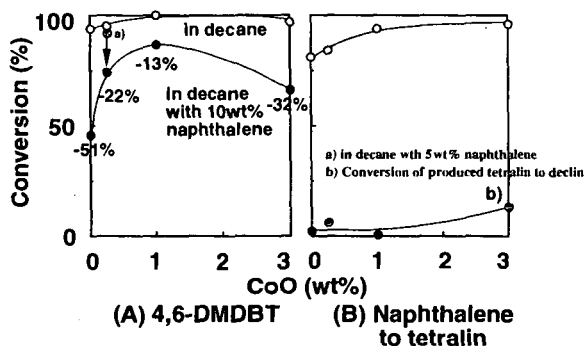


Fig.3 Inhibition with naphthalene of HDS reaction over CoMo catalysts.

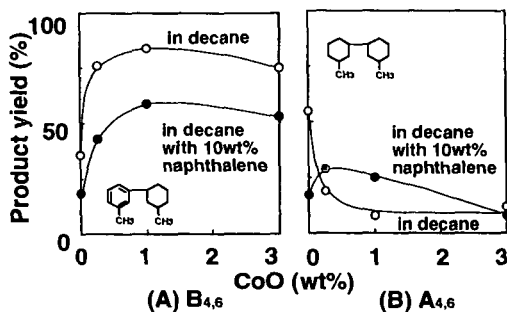


Fig.4 Major products from 4,6-DMDBT over CoMo catalysts.

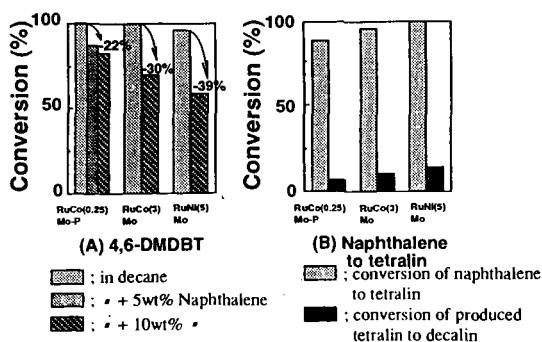


Fig.5 Inhibition with naphthalene for the HDS reaction of 4,6-DMDBT over Ru(0.75)-Co(0.25)-Mo-P, Ru(0.75)-Co(3)-Mo and Ru(0.75)-Ni(5)-Mo / Al<sub>2</sub>O<sub>3</sub>. (300°C-2.5MPa-2h, 4,6-DMDBT 0.1wt% + Nap 10wt% in decane, Catalyst content; 15 wt% )

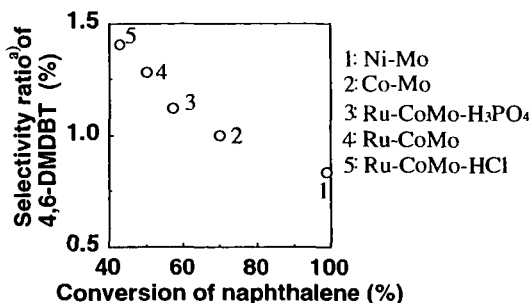


Fig.7 Effect of the additive on the HDS selectivity ratio of 4,6-DMDBT

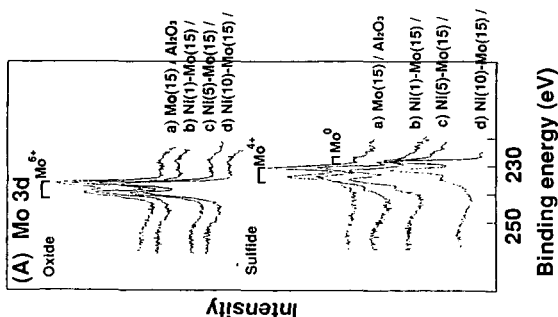


Fig.8 XPS spectra of MoS<sub>2</sub> based on catalysts before and after presulfiding

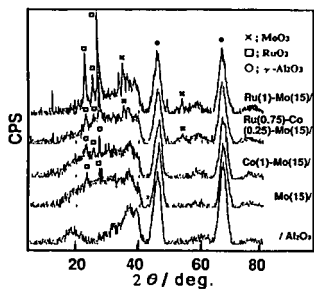
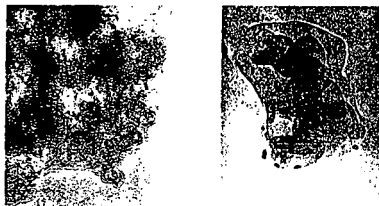


Fig.9 XRD spectra of MoS<sub>2</sub> based on catalysts before presulfiding

(a)

(b)



(c)

(a) (b) under 20K magnification  
(c) " " 50K "



Fig.10 HREM micrographs of sulfide  
Ru(0.75)-Co(0.25)-Mo(15) / Al<sub>2</sub>O<sub>3</sub>

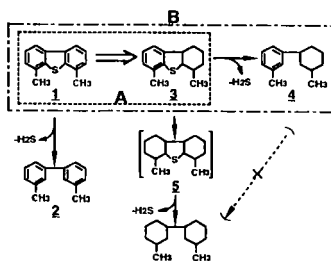


Fig.11 Reaction pathway of 4,6-Dimethyldibenzothiophene over Mo sulfide based on catalyst. ( 300°C-2.5MPa)